— IONIC EQUILIBRIUM —

TYPES OF ~~EQU~~ ELECTROLYTES :

A) **Strong electrolytes :**

Salts : NaCl, KCl, $CuSO_4$ | SA : H_2SO_4, HCl, HNO_3, $HClO_4$, HBr, HI
SB : LiOH, KOH, NaOH, $Ba(OH)_2$, CsOH, RbOH

→ Eg: Na_2SO_4, $NaHSO_4$, Conc. H_2SO_4, Conc. HNO_3, Conc. H_3PO_4, Conc. NaOH, $Ca(OH)_2$ etc.

→ $\alpha \simeq 100\%$; $\alpha = 1$

→ Doesn't form ionic equilibrium.

→ completely ionised in aqueous solution

B) **Weak Electrolytes :** $\alpha < 1$
$\alpha < 100\%$

→ Eg: CH_3COOH, HCOOH, all organic acid, NH_4OH, NH_3, PH_3, CH_3COONH_4, $HCOONH_4$ etc., H_2O
H_3BO_3 (Boric Acid), HCN, H_2CO_3, H_3PO_3, H_3PO_2

C) **Non electrolytes:**

→ Urea, glucose, sucrose, all monosaccharides, all disaccharides, etc ($i = 1$)

ACID- BASE CONCEPT:

A) **Arrhenius Concept** → Water → Neutral
Act as Solvent.

According to Arrhenius, those substance which release H^+ or H_3O^+ ion or acid.
$[H^+] = [H_3O^+]$

Eg: H_2SO_4, HCl, HNO_3, H_3PO_4 etc.

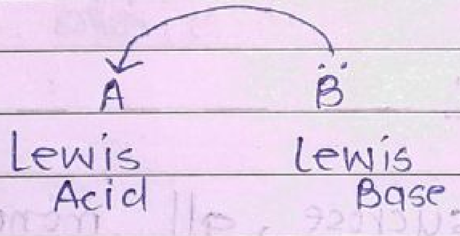
→ Those substance which release OH^- ion called Arrehenius Base.

Eg: $NaOH$, NH_4OH, $Ca(OH)_2$, $Ba(OH)_2$ etc.

Limitations:

- It doesnot justify acidic nature of $AlCl_3$, BF_3 etc. and basic nature of NH_3, PH_3, Amine (like CH_3NH_2, $C_2H_5NH_2$ etc.), CH_3OCH_3 etc.

B) Lewis Concept:



Lewis Acid: e^- Pair Acceptor (ELECTROPHILIC)
Lewis Base: Nucleophilic

→ According to Lewis, those substances which accept lone pair of electron are known as Lewis Acid while those substance which donates lone pair of electron are called Lewis Base

→ Eg: Lewis Acid

- Empty orbitals substance like PCl_3, $AlCl_3$, BF_3

→ Yaha in saare me octet complete nahi hote.

Strong Oxidising Agent → IA

- Central Metal atom in coordination cpds like
  $K_4[Fe(CN)_6]$
  └ Act as lewis acid.

- All strong Oxidising Agent act as lewis Acid.
  $KMnO_4$ (+7), H_2SO_4 (+6), HNO_3 (+5)
  $K_2Cr_2O_7$ etc.
  (H_2SO_4) └ strong lewis Acid than HNO_3.

- Positive charge speciee like Cu^{+1}, Fe^{+2}, Fe^{+3} etc.

→ Eg: Lewis Base

- Lone pair molecule / substance like CH_3, $CH_3\ddot{O}CH_3$, $\ddot{N}H_3$, $C_2H_5\ddot{O}H$ (ethanol), $R\ddot{N}H_2$, etc, H_2O

- All ligands in Coordination cpds like NH_3, CO, H_2O, CN^-, $C_2O_4^{-2}$, Ethylene diammine etc.

c) Bronsted - Lowrry Concept:

→ According to this concept, those substance which donate proton called Bronsted - Lowrry Acid while those substance which accept proton are called Bronsted-lowrry Base.

Eg:

$$NH_3 \xrightarrow{H^+} NH_4^+$$

B.L. Base [illegible] B.L Acid

$$CH_3COOH \xrightarrow{H^+} CH_3COO^-$$

Acid. Base

→ Here, pair of conjugated Acid and conjugated Base are obtained.

Eg:

$$\underset{\text{ACID 1}}{HCl} + \underset{\text{BASE-2}}{H_2O} \longrightarrow \underset{\text{ACID-2}}{H_3O^+} + \underset{\text{Base 1}}{Cl^-}$$

→ According to this concept, water (H_2O) is amphoteric in nature.

→ When water react with an acid, it act as basic while water react with bases, it act as acidic

$$\underset{\text{Base : 01}}{NH_3} + \underset{\text{Acid 2}}{H_2O} \longrightarrow \underset{\text{Acid 1}}{NH_4^+} + \underset{\text{Base 2}}{OH^-}$$

Abiya Amphoteric tyare j thase jyare eni paase 1 proton hase

Que: Write down the Conjugated Acid / Conjuga Base:

(A) HCO_3^-

$$HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$$

Base 1   Acid 2   Acid 1   Base 2

H_2CO_3 → Conjugated Acid

CO_3^{2-} → Conj. Base

(B) HS^- H_2S S^{2-}

(C) CO_3^{-2} HCO_3^- x

IONIC PRODUCT OF WATER OR IONIC CONSTANT OF WATER

→ It is denoted as **Kw**.

→ Water is weak electrolyte because only one molecule of water (approx) dissociate into its constituent ion from 10,000 of molecules.

$$H_2O(l) \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

or

$$K[H_2O] = [H^+][OH^-]$$

$$\boxed{K_W = [H^+][OH^-]}$$

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श्रीहरिकृष्णधाम (राष्ट्रनगर)

Note K_W at 25°C → 10^{-14}
K_W at 90°C → 10^{-12}

$[H^+] = [OH^-] = 10^{-7}$ at 25°C temperature.

$[H^+] = [OH^-] = 10^{-6}$ at 90°C temperature

Note
$[H^+] > [OH^-]$ (Acidic in Nature)
$[H^+] < [OH^-]$ (Basic in Nature)
$[H^+] = [OH^-]$ (Neutral)

$[H^+] > 10^{-7}$ (Acidic) (Like 10^{-6}, 10^{-5}, 10^{-4}, etc)
$[OH^-] > 10^{-7}$ (Basic)

RELATION BETWEEN IONIC PRODUCT OF WATER (K_W) AND DISSOCIATION CONSTANT OF WATER (K):

$$H_2O(l) \rightleftharpoons [H^+]\,[OH^-]$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$K_W = [H^+][OH^-]$

Wt. of 1 L ka mole $\Rightarrow \frac{1000}{18} = 55.5$

$$K = \frac{K_W}{55.5}$$

$$\boxed{K_W = K \times 55.5}$$

$K_W \Rightarrow 10^{-14}$ (25°C)

$K = \frac{K_W}{55.5}$

OR

$$\boxed{K = \frac{10^{-14}}{55.5}}$$

where $K \rightarrow$ dissociation constant of water.

Que: Find out the pH of following solution after

OSTWALD DILUTION LAW:

Ostwald is the first scientist to estabilished ionic equilibrium in weak electrolytes.

$$AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

	$AB(aq)$	$A^+(aq)$	$B^-(aq)$
Initial conc.	C	0	0
α	$(C - C\alpha)$	$(C\alpha)$	$(C\alpha)$

Acc. to law of Mass Action

Ionisation Constant; $K = \frac{[A^+][B^-]}{[AB^-]}$; $K = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$

If $\alpha <<< 1$, then

$1-\alpha \simeq 1$ → K = constant, At const. temperature

$$\boxed{K = C\alpha^2} \quad \text{or} \quad \boxed{\alpha = \sqrt{\frac{K}{C}}}$$

$$\alpha \propto \frac{1}{\sqrt{C}} \quad \left[C \propto \frac{1}{V}\right] \quad \boxed{\alpha \propto \sqrt{V}}$$

$$\boxed{H^+ = C\alpha}$$

☀ APPLICATIONS OF OSTWALD's DILUTION LAW: $K = C\alpha^2$

1. Ionisation / Dissociation Constant (K_a) for mono-basic Weak Acid (WA)

For calculation of pH of Weak Acid; first we find out $[H^+]$ ion concentration wrt degree of dissociation and Ka. After, then put the value in $pH = -\log H^+$

$$K_a = \frac{C\alpha^2}{(1-\alpha)} \; ; \; K_a = C\alpha^2$$

(ii) $[H^+]$

$$[H^+] = C\alpha = \sqrt{K_a \times C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$\boxed{[H^+] = C \times \sqrt{\frac{K_a}{C}}}$$

(iii) pH

$$pH = -\log [H^+]$$

$$\boxed{pH = \frac{1}{2} pK_a - \frac{1}{2} \log C}$$

→ K_b

2) Ionisation / Dissociation constant for Mono-acidic Weak Base (BOH)

$$BOH \rightleftharpoons B^+ + OH^-$$

	BOH	B^+	OH^-
Initial conc.	C	0	0
At equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

(i) $K_b = \frac{C\alpha^2}{(1-\alpha)}$; $K_b = C\alpha^2$

→ depends only on temperature.

(ii) $[OH^-]$

$$[OH^-] = C\alpha = \sqrt{K_b \times C}$$

$$[OH^-] = C \times \sqrt{\frac{K_b}{C}}$$

(iii) pOH

$$pOH = -\log [OH^-]$$

$$pOH = \frac{1}{2} pK_b - \frac{1}{2} \log C$$

※ pH

· pH is a scale to measure $[H^+]$ in a solution. The value of pH decide the acidic or basic nature of solution

0 —— Acidic —— <7< (Neutral) —— Basic —— 14

$pH = -\log H^+$ or $H^+ = 10^{-pH}$

$pOH = -\log [OH^-]$

$pH + pOH = 14$ at 25° C temp

$pKw = pH + pOH = 14$

Que: Calculate the pH of following solution:

- pH for Strong Acid

1) 0·01M HCl

Here, $H^+ = 0{\cdot}01M = 10^{-2}M$

$pH = -\log 10^{-2} = 2$

2) 0·005 M H_2SO_4

Here, $H^+ = 0{\cdot}005M = 5\times10^{-3}M$ $2\times0{\cdot}005$

(There are 2H so multiply $0{\cdot}005\times(2)$)

$pH = -\log[5\times10^{-3}]$
$= -\log 5 + \log 10^{-3}$
$= -(0{\cdot}6998) + 3$
$=$ ✗

$pH = -\log(H^+)$
$= \frac{10}{1000} = 10^{-2}$

$pH = -\log 10^{-2} = 2$

c) 0.005 N H_2SO_4

Normality = Molarity × n

$M = \frac{N}{n}$

$= \frac{5}{1000 \times 2} = 0.0025$

$[H^+] = 2 \times 0.0025$

$= \frac{5}{1000} = 5 \times 10^{-3}$

$pH = -\log[H^+]$

$= -\log(5 \times 10^{-3})$

$= -\log 5 + \log 10^{-3}$

$= -0.6998 + 3$

$= 2.3$

D) 0.02M H_3PO_3 : (Here, n = 2 so always Multiply 0.02 × (2))

$[H^+] = 0.02 = 2 \times 0.02$

$= 0.04$

$pH = -\log[H^+]$

$pH = -\log(4 \times 10^{-2})$

$pH = -\log 4 + \log 2$

$= -2\log(2) + \log(2)$

$= -(0.60 + 2)$

$= 1.4$

|| ॐ सर्वोपरिणे श्रीत्वमित्रायणायते नमः ||

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→ 10^{-5} se jyada diya ho to ye method se solve karne ka.

Que:

E) 10^{-6} M HCl

→ due to H_2O as HCl is very very dilute acid

$$pH = -\log(10^{-6}+10^{-7})$$

$$\log 10^{-7}\left(\frac{10^{-6}}{10^{-7}}+\frac{10^{-7}}{10^{-7}}\right)$$

$$\log 10^{-7}(10+1)$$

$$pH = -\log 10^{-7}(10+1)$$

$$= 7 - \log 11$$

$$pH = 7-1.04$$

$$= 5.96$$

F) 10^{-8} M HCl

$$pH = -\log(10^{-8}+10^{-7})$$

$$= -\log 10^{-8}(1+10)$$

$$= 8 - \log 11$$

$$= 8-1.04$$

$$pH = 6.96$$

G) 10^{-7} M HCl

x(2)

$$pH = -\log(10^{-7}+10^{-7})$$

$$pH = -\log 10^{-7}(1+1)$$

$$= 7-\log 2 = 7-0.3$$

$$= 6.7$$

Calculation of pH for STRONG BASE :

1) 0.01 M NaOH

$[OH^-] = 0.01 = 10^{-2}$

$pOH = -\log [OH^-] = -\log 10^{-2} = 2$

$pH + pOH = 14$

$pH = 14 - 2 = 12$

(Here, concentration of $H^+ = 10^{-12}$)

2) 0.036 M $Ca(OH)_2$

$[OH^-] = 0.036 \times 2$
$= 0.072$
$= 7.2 \times 10^{-2}$

$pOH = 2 - \log 7$
$= 2 - 0.845$
$= 1.155$

$pH + pOH = 14$
$pH = 14 - 1.15$
$= 12.85.$

$N_3 = [H^+]$

Calc. of pH after mixing strong Acid:

$$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$$
$$M_1V_1n_1 + M_2V_2n_2 = N_3(V_1 + N_2)$$

Que Calc. the pH of solution when 0.01M HCl (50 ml) mixed with 0.05M H_2SO_4 (50 mL).

(HCl) $N_1 = M_1 \times n = 0.01 \times 1 = 0.01$ N ; $V_1 = 50$ mL
(H_2SO_4) $N_2 = M_2 \times n = 0.05 \times 2 = 0.1$ N ; $V_2 = 50$ mL

$$N_1V_1 + N_2V_2 = N_3(V_1 + V_2)$$
$$(0.01)50 + (0.1)50 = N_3(100)$$
$$(0.5) + (5.0) = N_3(100)$$
$$\frac{5.5}{100} = N_3$$
$$55 \times 10^{-3} = N_3 = [H^+]$$

$$pH = -\log[H^+]$$
$$= -\log(55 \times 10^{-3})$$
$$= 3 - \log(11 \times 5)$$
$$= 3 - [\log 11 + \log 5]$$
$$= 3 - (1.04 + 0.69)$$
$$= 1.27$$

Calculation of pH after mixing Strong Bases

$$N_1V_1 + N_2V_2 = N_3(V_1+V_2)$$
$$M_1V_1n_1 + M_2V_2n_2 = N_3(V_1+V_2)$$

$N_3 = [OH^-]$ in final solution
$=$ Normality of final solution.

So, first calculate pOH after than pH.

Que. When 0.02 M NaOH (60 ml) mixed with 0.08M $Ca(OH)_2$ (20 ml). Then Calculate the pOH and pH of solution after mixing.

(NaOH) ; $N_1 = M_1 \times n = 0.02 \times 1 = 0.02N$; $V_1 = 60ml$
$[Ca(OH)_2]$; $N_2 = M_1 \times n = 0.08 \times 2 = 0.16N$; $V_2 = 20ml$

$$N_1V_1 + N_2V_2 = N_3(V_1+V_2)$$
$$0.02(60) + 0.16(20) = N_3(80)$$
$$\frac{2 \times 60}{100} + \frac{16 \times 20}{100} = N_3(80)$$
$$\frac{1.2 + 3.2}{80} = N_3$$
$$\frac{4.4}{800} = N_3 = 55 \times 10^{-3} = [OH^-]$$

$$pOH = -\log[OH^-] = 1.27$$

$$pH + pOH = 14$$
$$pH = 14.00 - 1.27 = \boxed{12.73}$$

Calculation of pH after dilution of SA + SB

$$N_1V_1 = N_2V_2$$
$$\frac{M_1V_1n_1}{V_2} = N_2$$

$V_2 \rightarrow$ final volume of solution

Que When 500 ml, 0·03 M H_3PO_2 diluted with 500 ml of H_2O. Then find out of pH of solution after dilution.

$$N_2[H^+] = \frac{0·03 \times 500 \times 1}{500 + 500} = 0·015 = 15 \times 10^{-3}$$

$$pH = -\log (15) \times 10^{-3}$$
$$= 3 - (\log 5 + \log 3)$$
$$= 3 - (0·69 + 0·47)$$
$$= 3 - (1·16)$$
$$pH = 1·84$$

Calculation of pH after mixing SA & SB (Neutralisation Rxn).

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$\frac{N_1V_1 - N_2V_2}{V_3} = N_3$$

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$$\frac{M_1V_1n_1 - M_2V_2n_3}{V_3} = N_3$$

Note · If gm eq of ACID = gm eq of Base

$(NV)_{Acid} = (NV)_{base}$ (pH = 7 Neutral)

· $(NV)_{ACID} > (NV)_{BASE}$; Acidic (pH < 7)

· $(NV)_{ACID} < (NV)_{BASE}$; Basic (pH > 7)

Que 2 DPP03 500 ml, 0·15M H_2SO_4 + 500 ml, 0·1M NaOH

$N_1V_1 = N_2V_2$

$\frac{0.15 \times 2 \times 500}{1000} = N_2$

$\frac{15 \times 10}{100 \times 10} = N_2 = 0.15 = 15 \times 10^{-2}$

$pH = 2 - (\log 3 + \log 5)$

$= 2 - (0.47 + 0.69)$

$= 2 - 1.16$

$= 0.84 \simeq 1$

Que 4 $40 cm^3, 0.1 M HCl + 10 cm^3, 0.45 M NaOH$

$N_1 = 0.1(1) = 0.1$; $V_1 = 40 cm^3 = 40 mL$

$N_2 = 0.45(1) = 0.45$; $V_2 = 10 cm^3 = 10 mL$

$$\frac{N_1V_1 - N_2V_2}{V_3 (V_1+V_2)} = N_3$$

$$\frac{0.1(40) - 0.45(10)}{50 (V_1+V_2)} = N_3$$

$$\frac{4 - 4.5}{50} = N_3 \Rightarrow N_3 = 0.01 = 10^{-2}$$

$$pOH = -\log OH = -\log(10^{-2}) = 2$$

$\therefore pH + pOH = 14$

$\Rightarrow pH = 14 - 2 = \boxed{12}$

Que 6 Sol. A ; pH = 3
+ Sol. B ; pH = 2
Vol. same
If both are mixed, then resultant pH of sol^n.

Calculation of pH for Weak Acid

Que6

$$HA \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

HA	H^+	A^-
C	0	0
$C - C\alpha$	$C\alpha$	$C\alpha$

$\therefore K_a = C\alpha^2$ or $\alpha = \sqrt{\frac{K_a}{C}}$ **

$H^+ = C\alpha$ or $H^+ = \sqrt{K_a \times C}$

$$pH = -\log (K_a \times C)^{1/2} = -\frac{1}{2} \log (K_a \times C)$$

Que02 DPP04 pH of 0.1 M CH_3COOH ($K = 1.80 \times 10^{-5}$ at $25°C$) will be:

$$pH = -\frac{1}{2} \log (1.8 \times 10^{-5} \times 0.1)$$

$$= -\frac{1}{2} \log (1.8) + \log 10^{-5} + \log 10^{-1}$$

$$= -\frac{1}{2} \log 18 + \log 10^{-1} + \log 10^{-5} + \log 10^{-1}$$

$$= -\frac{1}{2} (\log 9 + \log 2) + 1 + 5 + 1$$

$$= \frac{1}{2} (7 - 1.25) = \frac{5.75}{2} = \boxed{2.873}$$

Que6 pH of 0.1 M aq. solⁿ of WA = 3 (C = 0.1 M)
$\alpha = ?$

$H^+ = C\alpha$

$\alpha = \frac{H^+}{C} = \frac{10^{-3}}{0.1} = 10^{-2} = \frac{1}{100} = 0.01$

$= 0.01 \times 100 = 1\%$

Calculation of pH for Weak Base

$BOH \rightleftharpoons B^+(aq) + OH^-(aq)$

C	0	0
$C - C\alpha$	$C\alpha$	$C\alpha$

$K_b = C\alpha^2$

$\alpha = \sqrt{\frac{K_b}{C}}$

$OH^- = C\alpha$

$OH^- = \sqrt{K_b \times C}$

$pOH = -\log(K_b \times C)^{1/2} = -\frac{1}{2}\log(K_b \times C)$

Que 01 pH of 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)
DPP 4

$pOH = -\frac{1}{2}\log(K_b \times C)$

$= 2.873$

$pH + pOH = 14$

$pH = 14 - 2.873$

$pH = 11.1$

Que Calculate the pH for 0.2 M NH_4OH
[$pK_b = 3$] $C = 0.2$

[Formula Used: $pOH = pK_b\frac{1}{2} - \frac{1}{2}\log C$]

$pOH = \frac{1}{2} \times 3 - \frac{1}{2}\log 0.2$

$= \frac{3}{2} - \frac{1}{2}\log(2 \times 10^{-1})$

$= \frac{3}{2} - \frac{1}{2}(\log 2) + \log 10^{-1}$

$= 1 \times 0.30 + 1$

$pOH = 1.3$

$pH = 14.00 - 1.30$

$= 12.7$

$\begin{array}{r} 14.0 \\ -1.3 \\ \hline 12.7 \end{array}$